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Rate Constant for the Reaction of NO2 with Sulfur(IV) over the pH Range 5.3-13 (Journal Version)

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16. ABSTRACT

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JOURNAL ARTICLE

Rate Constant for the Reaction of NO_2 with Sulfur(IV) over the pH Range 5.3–13

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■ Rate constants have been determined for the reactions of NO_2 with SO_3^{2-} and HSO_3^- in aqueous solutions. The rate constant increases from about 1.2×10^7 M^{-1} s^{-1} near pH 5 to 2.9×10^7 M^{-1} s^{-1} at pH 13. The reaction appears to involve the formation of an intermediate complex that may undergo subsequent reaction with NO_2 to yield the ultimate products or may react with other substrates present. The formation of a long-lived intermediate would have implications on the chemistry of flue gas scrubbers and on luminol-based NO_2 detectors.

Introduction

Air pollution by both sulfur dioxide and nitrogen oxides has been recognized as major problems almost since the start of the industrial revolution. These pollutants have been in the spotlight more recently as precursors to the strong mineral acids HNO_3 and H_2SO_4 in precipitation. Yet, an effective, reliable, and inexpensive technique for removing these gases from emission sources, mainly coal-fired power plants, remains an elusive goal (*1*). Although a considerable amount of work has been done on the development of water-based flue gas scrubbers, there are major gaps in our understanding of the basic chemistry involved in their operation, particularly the free radical chemistry. Of particular importance are the reactions of the free radical NO_2, which may be formed in the gas phase through normal combustion reactions or deliberately formed in the flue gas to aid in the removal of NO_x. In a combined SO_x/NO_x scrubber, the NO_2 radical may react with dissolved S(IV) [SO_2(aq), HSO_3^-, or SO_3^{2-}], effecting the removal efficiency of both.

An improved understanding of the underlying chemistry of the atmospheric conversion of SO_2 to SO_4^{2-} is also needed in order to allow the development of reliable atmospheric models. In atmospheric droplets, the reaction of NO_2 with HSO_3^- may serve as an additional pathway for acidification of the droplet. The reaction of NO_2 with SO_3^{2-} may also play an important role in the chemistry of the luminol-based chemiluminescence detector for NO_2. The addition of Na_2SO_3 has been found not only to reduce the interference from O_3 but also to increase greatly the sensitivity of that detector (*2*, *3*).

There has been some work on the effect of NO_2 on HSO_3^-/SO_3^{2-} oxidation (*4–8*) and the effect of SO_3^{2-} autoxidation on the absorption of NO_2 into an aqueous solution (*9*). Of particular interest is the observation that while NO_2 will oxidize SO_3^{2-}, it does not initiate SO_3^{2-} autoxidation (*8*) (which is a free radical chain reaction) (*10*). Also, it is interesting to note that NO serves as an inhibitor of SO_3^{2-} autoxidation (*6*) and that the efficiency of NO_2 absorption into SO_3^{2-} solutions decreased if autoxidation is permitted (*9*).

Recently, we investigated the reactions of NO_2, generated by pulse radiolysis in aqueous solutions, with several organic and inorganic reactants (*11*). The pulse radiolysis apparatus employed in that study could operate only in a single-shot mode. This makes it difficult to follow very small absorbance changes. Since the optical absorption due to NO_2 is very weak, its reactions were followed by monitoring a product radical from the other reactant. For the reaction with SO_3^{2-}, however, this was not possible, so the rate constant had to be measured relative to the reaction of NO_2 with phenol. The results were not completely satisfactory, and only an approximate number was reported and only at pH 12.1. In this work, we have employed a pulse radiolysis apparatus with signal averaging, which has allowed us to monitor the decay of NO_2 directly and to measure rate constants for the reaction of NO_2 with SO_3^{2-} and HSO_3^- over the pH range 5.3–13.

Experimental Section

The pulse radiolysis apparatus, capable of repeated pulses under computer control, will be described in detail elsewhere (*12*). It employs a Van de Graaff accelerator which, in these experiments, delivers 0.5-μs pulses of 2.8 MeV electrons to the reaction cell. The temporal history of a reactant or product is monitored by absorption spectroscopy. A decay curve from each individual pulse is recorded by a transient analyzer and transferred to the

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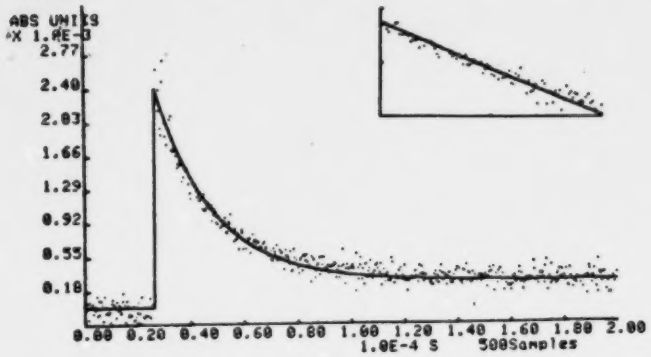


Figure 1. Decay of absorbance due to NO_2 at 400 nm. Solution containing 10 mM $NaNO_2$ and 1.5 mM Na_2SO_3 at pH 11.75. Average of 50 pulses. Insert: log Abs vs t.

computer. If the dose delivered by the Van de Graaff accelerator is within a preset range, the data are added to memory. This procedure is repeated enough times to produce a signal sufficient for analysis. The data are then analyzed by a linear least-squares program.

Reagent-grade chemicals were used as supplied; water was purified by an ion-exchange system. Separate solutions of $NaNO_2$ and of several concentrations of Na_2SO_3 were prepared. The solutions were saturated with N_2O and mixed just upstream of the 2 cm long irradiation cell, making use of a peristaltic pump. This procedure prevented possible complications due to the reaction of HNO_2 with HSO_3^-.

The irradiation of aqueous solutions at pH 3–13 produces the hydroxyl radical and the hydrated electron in similar concentrations, along with a small (<10%) yield of hydrogen atoms. In N_2O saturated solutions, the hydrated electron is converted to OH:

$$H_2O \rightarrow \rightarrow \rightarrow e_{aq}^-, H, OH \qquad (1)$$

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH + OH^- \qquad (2)$$

The OH radical then reacts with NO_2^- to produce NO_2 ($k \sim 1 \times 10^{10}$ M^{-1} s^{-1}) (*13*):

$$OH + NO_2^- \rightarrow OH^- + NO_2 \qquad (3)$$

Under our experimental conditions, about 5 μM NO_2 typically is produced. With no added solute, NO_2 equilibrates with its dimer N_2O_4 ($k = 4.5 \times 10^8$ M^{-1} s^{-1}; $K = 1.53 \times 10^{-5}$ M) (*14*), which then disproportionates to NO_2^- and NO_3^- (*15*).

Results and Discussion

The pulse irradiation of a N_2O saturated NO_2^- solution produced a very weak optical absorption due to NO_2 with maxima at 400 and 420 nm. We have not attempted to determine the absorptivity quantitatively, but our results appear compatible with the value of $\epsilon = 200$ M^{-1} cm^{-1} at 400 nm reported previously (*14*). To obtain an adequate signal for analysis, from 20 to 200 pulses were needed, depending upon conditions. Rate constants for the decay of the signal due to NO_2 were determined upon the addition of a great excess of S(IV). A sample experimental decay curve is given in Figure 1. In all cases, good first-order behavior was observed. Replicate runs were made at each S(IV) concentration, and typically, four concentrations between 5×10^{-4} and 2×10^{-3} M were employed to derive a second-order rate constant (Figure 2). Rate measurements were carried out over the pH range 5.3–13, with the results given in Table I and plotted

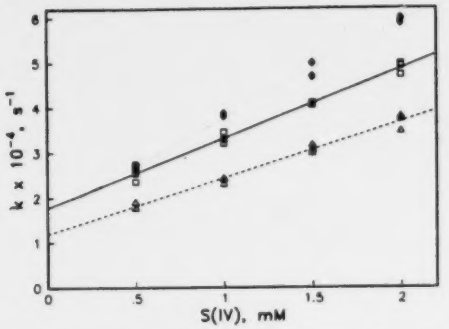


Figure 2. Concentration dependence of the first-order rate constant for the reaction of NO_2 with S(IV). Triangles, pH 5.3; squares, pH 6.7, 0.5 M phosphate buffer; diamonds, pH 11.75.

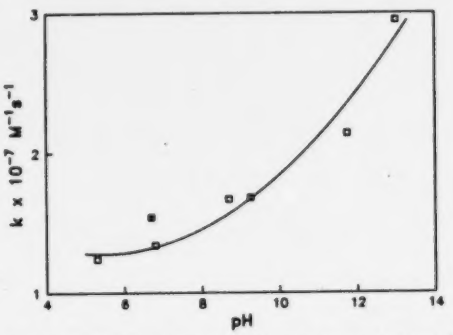


Figure 3. Dependence of the second-order rate constant for the reaction of NO_2 with S(IV) on pH. Solid square, 0.5 M phosphate buffer.

Table I. Rate Constants for the Reaction of NO_2 with SO_3^{2-}/HSO_3^-

pH	$k \times 10^{-7}$, M^{-1} s^{-1}	conditions
5.3	1.24	1 mM phosphate
6.7	1.54	0.5 M phosphate
6.8	1.34	$NaHSO_3 + Na_2SO_3$, no buffer
8.7	1.67	1 mM borate
9.3	1.68	1 mM borate
11.8	2.14	1 mM phosphate + KOH
13	2.95	0.1 M KOH

against pH in Figure 3. Rate measurements were not attempted at lower pH to avoid complications from the reaction of HNO_2 with HSO_3^-.

The pK for the deprotonation of bisulfite

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \qquad (4)$$

is 7.19 (*16*). In general, free radicals react with SO_3^{2-} more rapidly than with HSO_3^- (*10*, *17*). This reflects the decrease in one-electron redox potential in going from HSO_3^- to SO_3^{2-} and leads to an inflection in the rate constant around the pK for HSO_3^-, with a lower rate constant below pH 7.19 and a higher value above that pH. Yet, in Figure 3 there is no indication of any inflection around that point. This suggests that the change in rate constant with pH does not result simply from the increased amount of SO_3^{2-} but involves general or specific base catalysis. Indeed, although the increase in rate constant with pH appears very sharp, the total increase in going from pH 5.3 to pH 13 is only about a factor of 2.5.

Although the change in rate constant with pH is not coincident with the transition from HSO_3^- to SO_3^{2-}, there is certainly an increase in rate constant with pH. To

investigate the possible importance of a general base catalyzed path, we determined the rate constant in the presence of 0.5 M phosphate buffer. The rate constant increased, but only slightly. This suggests that the increase in rate constant is associated primarily with the increase in OH^- concentration. Since the increase in rate constant with pH is so small, we have not attempted to derive an OH^--dependent rate expression.

In our earlier work on the reaction of NO_2 with SO_3^{2-}, we concluded that the reaction did not take place by a simple electron transfer. We arrived at this conclusion by comparing the rate constants for reactions of NO_2 with comparable reactions of ClO_2. In all other cases, where electron transfer was confirmed by observing the product radicals, the reaction of ClO_2 with a substrate was faster than the reaction of NO_2. The reaction of NO_2 with SO_3^{2-}, however, was faster than for ClO_2. The present results support that conclusion, since if the reaction were a simple electron transfer, the change in rate constant with pH should reflect the relative amounts of SO_3^{2-} and HSO_3^-.

There is also other information in the literature that, in conjunction with the present observations, sheds further light on the nature of this reaction. First is the observation, mentioned above, that whereas NO_2 can oxidize HSO_3^- or SO_3^{2-} directly, it does not appear to initiate their autoxidation. Second, the products and stoichiometry suggest that the overall reaction is mainly (*7*)

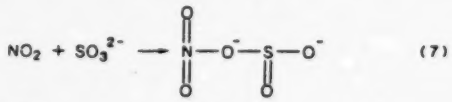
$$2NO_2 + HSO_3^- + H_2O \rightarrow 2NO_2^- + 3H^+ + SO_4^{2-} \quad (5)$$

with the yield of NO_2^- relative to HSO_3^- consumed 1.5 ± 0.4 and the yield of H^+ 2.5 ± 0.4. There appeared to be essentially no NO or NO_3^- produced. Third, the rate constant ($d[H^+]/dt$) determined by bubbling NO_2 through a HSO_3^- solution (>2×10^6 M^{-1} s^{-1} at pH 6.4 and 1.4×10^5 M^{-1} s^{-1} pH 5) (*18*) was much lower than the rate constant determined here. That work also showed that the reaction was not second order in NO_2, as the stoichiometry would suggest. Finally, it was observed that there was a small induction period in the generation of H^+ and that the generation of H^+ would continue for several minutes after NO_2 had been purged from the solution.

In our earlier work, we suggested that the reaction was a simple oxygen-atom transfer:

$$NO_2 + HSO_3^- \rightarrow NO + SO_4^{2-} + H^+ \quad (6)$$

The observations summarized above suggest that this is not likely to be the case. Rather, our observations and these other results suggest that the initial step involves the formation of an addition complex, which can undergo subsequent reaction with further NO_2:



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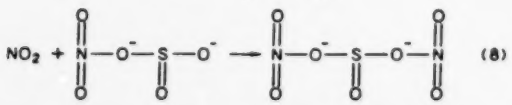
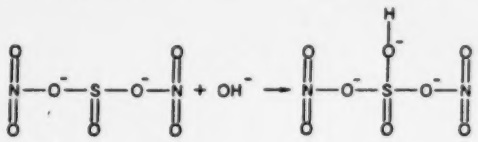


(8)

This second intermediate, which is potentially long lived, can then decompose, possibly in a base-catalyzed reaction, to NO_2^- and SO_4^{2-}:

In our experiments, the low initial NO_2 concentration (<10^{-5} M) will probably ensure that reaction 7 predominates. The occurrence of reaction 8 cannot be ruled out completely, however, but the very good first- and second-order plots (Figures 1 and 2) suggest that it is not important. Therefore, the rate constant we measure should correspond to the formation of the first complex. Indeed, there does seem to be a very small residual absorption at long time (Figure 1) that could be due to this complex. The production of acid upon bubbling NO_2 through a HSO_3^- solution, however, requires reactions 8–10 and would be expected to be much slower, as observed (*18*).



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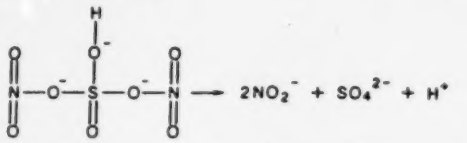

(10)

Relatively slow secondary steps also would be expected to lead to an induction period for the production of acid and the continued production of acid after the NO_2 was removed.

There is certainly considerable precedence for an addition reaction in the interactions of sulfite and bisulfite with nitrogen oxides and their anions. Nitrous acid reacts with bisulfate, first to form nitrososulfonic acid (*19*), which can then react further with bisulfate to form hydroxylaminedisulfonate (*20*):

$$HNO_2 + HSO_3^- \rightarrow ONSO_3^- + H_2O \quad (11)$$

$$ONSO_3^- + HSO_3^- \rightarrow HON(SO_3)_2^{2-} + H_2O \quad (12)$$

This product may hydrolyze or react with additional HSO_3^- to form aminetrisulfonate:

$$HON(SO_3)_2^{2-} + HSO_3^- \rightarrow N(SO_3)_3^{3-} + H_2O \quad (13)$$

In these reactions, three sulfites substitute onto the nitrogen, with the elimination of water. The reaction of nitric oxide with sulfite (*21*, *22*), however, appears to be more similar to what we are proposing here for nitrogen dioxide:

$$NO + SO_3^{2-} \rightarrow ONSO_3^{2-} \quad (14)$$

$$NO + ONSO_3^{2-} \rightarrow {}^-ON(NO)SO_3^- \quad (15)$$

$${}^-ON(NO)SO_3^- \rightarrow N_2O + SO_4^{2-} \quad (16)$$

In an atmospheric droplet, the fate of the initial intermediate formed from the reaction of NO_2 with SO_3^{2-} might not be simply to react with another NO_2, since that radical will be at such a low concentration in the droplet. The compound might serve as a one-electron oxidant, leading to the formation of nitrososulfuric acid. In a flue gas scrubber, particularly when the gas-phase NO is converted to NO_2, the intermediate is much more likely to react with additional NO_2 due to its much higher concentration. Confirmation of the production of this intermediate and information on its chemical behavior are needed to fully assess its role in these systems.

The formation of a reactive intermediate in the reaction of NO_2 with SO_3^{2-} might also help explain the role of added Na_2SO_3 on the operation of a luminol-based NO_2 detector. The reaction of SO_3^{2-} with O_3 is a simple oxygen-atom transfer (*23*), leading to unreactive products:

$$O_3 + SO_3^{2-} \rightarrow O_2 + SO_4^{2-} \quad (17)$$

This explains the ability of SO_3^{2-} to reduce the interference due to O_3. When NO_2 is dissolved into a luminol solution, its reaction with luminol is in competition with the removal

of NO_2 due to disproportionation. If a large concentration of SO_3^{2-} is present, the NO_2 will react to form an intermediate. This intermediate, then, can proceed to react with the luminol, leading to chemiluminescence. An investigation into the nature of this intermediate would be useful in predicting possible complications in the luminol-based NO_2 detector.

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Registry No. NO_2, 10102-44-0; NO_x, 11104-93-1.

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